

PROPIONIC ACID

BY THE AIR OXIDATION OF PROPIONALDEHYDE

Engineering
and
Process
development

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A laboratory investigation was made of the oxidation of propionaldehyde to propionic acid, a useful intermediate in the preparation of cellulose esters and fungicidal salts.

Comparative studies of cobalt and manganese propionates as catalysts for the liquid phase oxidation of propionaldehyde indicated the manganese salt to be superior to the cobalt salt, its optimum activity being reached at a concentration of 50 to 100 parts of metal per million parts of aldehyde. In the presence of 4 to 6% of water, conversions of propionaldehyde to propionic acid were increased about 25% in an arbitrarily fixed reaction time. A moderate improvement in yield also resulted. Under the best conditions the conversion of propionaldehyde was about 75% and the yield of propionic acid based on propionaldehyde consumed was approximately 90%.

These results show that, with suitable catalysts, air oxidation is a good method for converting propionaldehyde to propionic acid.

ALTHOUGH the oxidation of aldehydes to carboxylic acids is a well-known reaction, very few data of a specific nature have been published on the preparation of propionic acid from propionaldehyde. Most of the published work appears in the patent literature and these patents deal chiefly with the preparation of acetic acid or acetic anhydride.

One study of the oxidation of propionaldehyde with pure oxygen in the presence of manganese has been reported, but the variations in quantity of catalyst were very limited and only two experiments were listed in which air was used as a source of oxygen (1). The yields (corrected for recovered aldehyde) from these two experiments were 55 and 66%, and the maximum yield reported for experiments in which pure oxygen was used was 84.5%. Among the numerous catalysts that have been described for use in either liquid or vapor phase oxidations, as applied to a broad group of compounds, are carbon, silica gel, platinum, copper, copper oxide, and salts of aluminum, chromium, vanadium, manganese, cobalt, nickel, cerium, antimony, uranium, and bismuth. Of these, manganese and cobalt salts were indicated to be the most suitable for liquid phase reaction and were therefore studied in the present work.

PREPARATION OF CATALYSTS

Both the manganese and cobalt were used in the form of their propionic acid salts, with stock solutions of the salts in propionic acid being prepared so that the desired amount of catalyst could be conveniently added to the reaction system.

Manganese propionate was prepared by warming metallic manganese and propionic acid until the metal was completely dissolved. A 1% solution of manganese propionate was used in the first experiments and a 10% solution in the later work.

Cobalt propionate was prepared by the reaction of a sufficient amount of cobaltous hydroxide with propionic acid to give a 1% solution. The cobaltous hydroxide was prepared by precipitation from cobaltous nitrate solution with sodium hydroxide.

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APPARATUS AND PROCEDURE

Propionaldehyde and catalyst, contained in a 3-necked 500-ml. glass flask were pumped through a 7-mm. glass tube to the top of a 3 foot \times 1 inch column packed with $\frac{1}{8}$ -inch glass Raschig rings and returned to the flask against a countercurrent flow of air. The air, which was supplied by a compression pump, was metered and then scrubbed with sulfuric acid and soda-lime before being bubbled into the liquid in the reaction flask. The effluent was passed through two aldehyde condensers that were cooled with solid carbon dioxide and arranged in such a manner that the condensate could be continuously returned to the reaction system.

A stainless steel laboratory centrifugal pump was used to circulate the reaction liquid. Stainless steel withstood corrosion, but the cast-iron nipples with which the pump was originally equipped had to be removed, because the iron propionate that was formed interfered with the activity of the catalysts that were being studied.

Except in a few cases, no attempt was made to control the reaction temperature. Usually the oxidation was started at room temperature and within a short time, providing the catalyst was functioning satisfactorily, the temperature rose to between 40° and 50° C. Because propionaldehyde boils at 49° C., the cooling effect of the reflux liquid prevented the temperature from going higher. The temperature gradually decreased as the final stage of the oxidation was approached.

CATALYST INVESTIGATION

Before other reaction variables were investigated, a study was made to determine the relative merits of cobalt and manganese as catalysts and to establish the optimum use concentrations.

The charge for each experiment was 290 grams (5 moles) of propionaldehyde and sufficient propionic acid solution of catalyst to give the desired concentration. Sixteen cubic feet of air (approximately 6.7 gram-atoms of O) were passed into the system over approximately a 5-hour period. After a sample of the crude reaction mixture had been titrated to determine the maximum conversion to propionic acid, the products were distilled through an 18-inch column of 24 mm. diameter packed with $\frac{1}{8}$ -inch glass helices. Three fractions were taken: (1) a propionaldehyde cut up to 75° C., (2) an intermediate cut distilling between 75° and 120° C., and (3) a propionic acid fraction distilling between 120° and 141° C. The last fraction was titrated to determine its actual content of propionic acid.

Data on the catalyst studies are given in Tables I and II. The amount of catalyst is given in parts of metal per million parts of propionaldehyde. The percentage conversion to propionic acid is the percentage of the aldehyde charged that appeared as propionic acid in the product fraction of the distillation. The yield values make allowance for the recovered propionaldehyde. The yields based on titration of the crude products are not shown, but these data indicated that distillation losses were about 5%.

With no catalyst, very little oxidation occurred, but with only 7 to 10 p.p.m. of manganese or cobalt the reaction proceeded rapidly. The percentage conversion reached a maximum at about 50 p.p.m. and there appeared to be no advantage from the use of larger amounts. Manganese proved to be the better

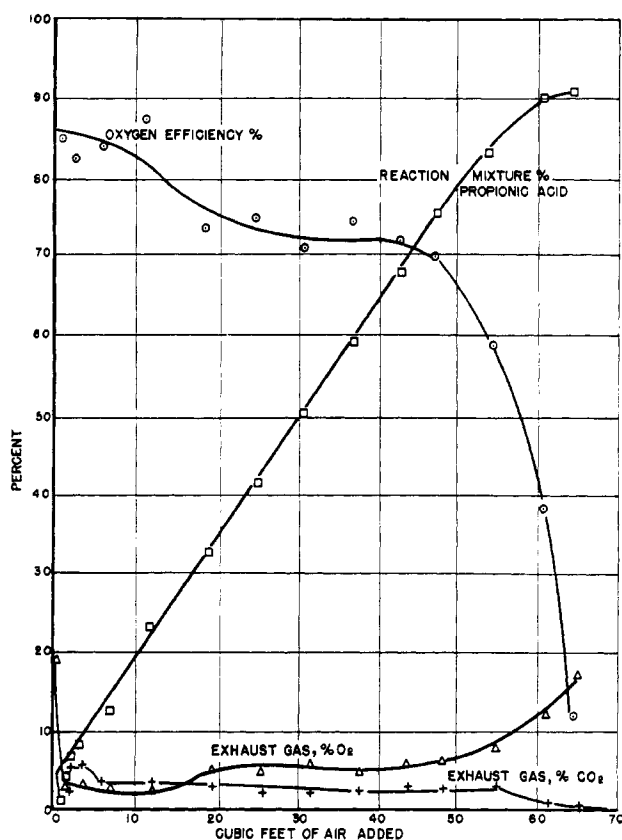


Figure 1. Carbon Dioxide and Oxygen Contents of Off-Gases from Air Oxidation of Propionaldehyde

catalyst, as the conversion of aldehyde under optimum conditions was about 60% as compared with 40% for cobalt.

VARIABLES AFFECTING OXIDATION IN PRESENCE OF MANGANESE PROPIONATE

From each of the experiments of the previously described catalyst study an intermediate fraction amounting to 3.5 to 5% of the charge was obtained that distilled between 75° and 120° C. indicating some side reactions. When an accumulation of these intermediates was worked up by distillation, water was isolated as a major component, the amount corresponding to about 0.04 mole per mole of aldehyde consumed. The expected accompanying product of overoxidation, carbon dioxide, was found to be present in the off-gases.

To improve yields, several modifications in reaction conditions as well as the effect of several additives and diluents were studied with manganese propionate serving as a catalyst. The procedure described in the previous section on catalysts was followed. From this work it was found that the use of a small amount of water as a propionaldehyde diluent was beneficial. The results of these experiments are given in Table III.

TABLE I. MANGANESE PROPIONATE CATALYST

Run No.	Amount of Catalyst, P.P.M.	Conversion to Propionic Acid, %	Yield, %
1	None	7.6	25.4
2	6.9	41.2	73.0
3	10	39.4	67.0
4	15	50.4	69.0
5	25	54.6	72.5
6	50	60.0	80.0
7	75	58.0	78.0
8	100	60.0	9.0
9	500	55.2	74.3

TABLE II. COBALT PROPIONATE CATALYST

Run No.	Amount of Catalyst, P.P.M.	Conversion to Propionic Acid, %	Yield, %
1	25	39.0	63.0
2	50	42.0	71.0
3	100	41.6	70.0
4	500	41.6	68.0

TABLE III. REACTIONS EMPLOYING WATER AS A DILUENT (Manganese propionate catalyst)

Run No.	Amount of Catalyst, P.P.M.	Water, %	Conversion to Propionic Acid, %	Yield, %
1	50	4	74.4	82.0
2	100	4	67.8	79.0
3 ^a	50	4	78.6 (74.6) ^b	88.5 (84.0) ^b
4 ^a	50	4	71.2 (67.6) ^b	85.0 (80.7) ^b
5	50	6	77.0	87.0
6 ^a	50	6	76.0 (72.2) ^b	91.5 (86.9) ^b
7 ^a	50	6	71.2 (67.6) ^b	88.0 (83.6) ^b
8	50	10	38.8	77.5

^a In these reactions the residue from the distillation of the product from the previous reaction was used to compensate for distillation losses.

^b Figures in parentheses have been multiplied by a factor of 0.95 to place compensated runs on the same basis with runs to which no distillation heel was added.

A comparison of the data with those of Table I indicates that water in the amount of 6% based on propionaldehyde charged resulted in yields of 84 to 87% as compared with yields of 78 to 80% when no water was added. Also it is shown that conversions were approximately 25% greater when 4 to 6% of water was employed. Too much water was found to be detrimental, as the conversion was approximately halved in going from 6 to 10% of water.

The following modifications and changes in reaction conditions were tested, but none resulted in any improvement:

1. Hydroquinone and tributylamine oxide as additives
2. Carbon dioxide in concentrations up to 60% as an air diluent
3. Fortification of the air with up to 50% oxygen
4. An initial concentration of 25% of propionic acid
5. An operating temperature of 20° C. (instead of 40° to 50° C.)
6. Reducing the rate of air input by 50%

In order to determine whether or not oxidation of carbon dioxide and water occurred at a constant rate during the reaction, a larger scale experiment (25 moles of aldehyde, 64 cubic feet of air) was set up in such a manner that the off-gases could be sampled periodically and analyzed for percentage of carbon dioxide and oxygen. It was hoped from this study that a stage in the reaction would be found at which the rate of carbon dioxide formation was negligible. If such a point could be found, it was thought that by removing acid at its rate of formation and continuously stripping and recycling unreacted aldehyde, overoxidation might be largely avoided. These data are plotted in Figure 1, along with data from a parallel experiment showing the change in acid concentration as determined by titration of samples that were periodically removed from the system. Also shown is an oxygen efficiency curve that represents the percentage consumption of the oxygen contained in the air.

The curves show that an appreciable amount of carbon dioxide was produced throughout the entire course of the reaction. Both the percentage of carbon dioxide formed and the percentage of oxygen consumed were at their highest points during the first part of the reaction. Between acid concentrations of about 20 and 75% the percentage of carbon dioxide was 2.0 to 3.5% and the oxygen efficiency was 68 to 82%. It is indicated that excessive oxidation cannot be avoided by regulation of the acid concentration.

LITERATURE CITED

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